

# Advanced Mass Spectrometer for Atmospheric Monitoring

## SERDP CP-192

### FY98 Final Report

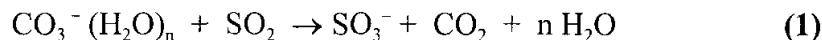
Air Force Research Laboratory  
Hanscom Air Force Base, Massachusetts

**Project Background:** The Clean Air Act Amendments of 1990 listed a wide variety of toxic and hazardous compounds whose emissions into the atmosphere needed to be monitored and reduced. At that time, there was no single instrument or measurement technique available to detect and quantify the concentrations of these species in the atmosphere. To meet the requirements of the CAAA, novel instrumentation for reliable and robust trace gas detection was required.

**Objective:** The objective of the Advanced Mass Spectrometer for Atmospheric Monitoring SERPD project was to develop Chemical Ionization Mass Spectrometry (CIMS) into a versatile, extremely sensitive, highly selective, and rugged field instrument for trace gas detection. The Air Force Research Laboratory at Hanscom AFB has a forty year history of successful mass spectrometric measurements of atmospheric ion and neutral composition. The Laboratory also has an international reputation in ion chemistry. The CIMS technique brought these two areas of expertise together.

**Technical Approach:** In the CIMS technique, trace neutral species are converted to unique ions by ion-molecule reactions in a high velocity flow. The product ions are then detected by a sensitive mass spectrometer. The selectivity of the technique comes from the choice of suitable precursor ions that react with trace species of interest to give product ions that are stable and uniquely traceable to the presence of those neutral species. The precursor ions do not react strongly with the major atmospheric species, significantly reducing the possibility of interferences. The sensitivity is due to the fact that ion-molecule reactions are extremely fast, often occurring on every collision.

The CIMS ion chemistry for  $\text{SO}_2$  is based on  $\text{CO}_3^-$  hydrates as the source ions and consists of the following ion-molecule reactions:



followed immediately by



Because no other reactions of  $\text{CO}_3^-$  ions with atmospheric trace neutrals give product ions

## Report Documentation Page

*Form Approved  
OMB No. 0704-0188*

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1. REPORT DATE <b>1998</b>	2. REPORT TYPE	3. DATES COVERED <b>00-00-1998 to 00-00-1998</b>		
4. TITLE AND SUBTITLE <b>Advanced Mass Spectrometer for Atmospheric Monitoring</b>			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Air Force Research Laboratory, Hanscom AFB, MA, 01731</b>			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>14</b>
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>		
19a. NAME OF RESPONSIBLE PERSON				

at the same mass as  $\text{SO}_5^-$ , detection of ion signal at a mass of 112 amu confirms the presence of  $\text{SO}_2$ . Hydration of the  $\text{CO}_3^-$  source ions is due to association reactions with water in the main flow tube. The variation of the reaction rate with  $\text{SO}_2$  as a function of the degree of hydration of the source ions has been studied in our laboratory. The results show negligible sensitivity to the amount of hydration in the present experiments. Furthermore, because the trace neutral concentrations are determined by in-flight calibrations and not by calculations based on kinetic parameters, the source ion hydration is accounted for directly.

The AFRL CIMS instrument is shown schematically in Fig. 1 in its T-39 configuration. The main components are 1) the gas sampling system, 2) the flow tube and flow diagnostic instruments, 3) the ion source, 4) the dryer and heated inlet for declustering ions, 5) the mass spectrometer, and 6) the calibration system. The entire instrument including power supplies, interface electronics, mounting racks, and all vacuum hardware is a self-contained, 60 x 70 x 100 cm, package weighing ~125 kg. The methods for sampling the exhaust gas were different for the test cell measurements and the near field chases and will be described separately. Most of the other instrument components were common to both experiments. Although the AFRL CIMS is conceptually similar to other CIMS instruments, there are several important differences in the details of the ion source position, calibration methods, etc. that are highlighted here.

***Gas Sampling System and Flow Tube Configuration.*** In the NASA Lewis altitude test cell experiments, the exhaust properties of the F-100 engine were measured with an array of probes mounted on a cross-shaped rake 21 cm behind the exit plane of the engine. The CIMS instrument sampled exhaust gas through three extractor probes on the lower part of the vertical probe rake. The probes were located 5.1 cm, 10.2 cm, and 15.2 cm below the engine axis and within the core exhaust flow. One meter from the rake, the sample lines from the three probes were joined into a single 0.64 cm o.d., 7.3 m long stainless steel line which transported the exhaust to the CIMS. The sampling lines were heated to 150 C to prevent loss of condensable gases on the walls. The sample lines were also coated with siloxane-covered glass to minimize sticking of  $\text{HNO}_3$  to the walls.

The exhaust effluent was drawn into the CIMS flow tube by the pressure drop across a siloxane-coated, 0.32 cm o.d., 7.5 cm long stainless steel capillary. The capillary restricted the exhaust flow to 4 – 15 slm. The main flow tube carried a fast flow of 120 slm of dry nitrogen mixed with the exhaust at a total pressure of 37 torr and ~53 m/s flow velocity. The dilution of the exhaust gas by typically a factor of six prevented saturation of the CIMS instrument. Running the instrument at constant flow tube pressure also eliminated the pressure dependence of the instrument's sensitivity. The exhaust end of the flow tube was pumped by a 100 cfm mechanical pump. These conditions were chosen to maximize the CIMS sensitivity and to maintain adequate exhaust effluent flow over the entire simulated altitude range of the test cell.

In the T-39 flight configuration, the flow tube was connected directly to a forward-facing air sampling scoop. The gas was carried undiluted down the flow tube by the ram pressure of the aircraft velocity. The gas exited the flow tube through a second, rearward-facing tube located slightly aft of the inlet. The sampling inlets for both the CIMS and the suite of instruments from NASA Langley (a non-dispersive infrared  $\text{CO}_2$  detector and several aerosol detectors) were

mounted in a 30 cm x 30 cm removable panel in the forward half of the T-39's roof. This insured that all instruments sampled the same regions of the exhaust plume at the same plume age.

On the T-39, the flow tube could be isolated from the atmosphere with valves at both ends in order to test the instrument on the ground and to keep the flow tube clean. The throttle valve at the downstream end was also used to adjust the flow velocity. During SNIF-3, the flow velocity was typically 70 m/s giving a Reynolds number of greater than 50,000 and a flow well into the turbulent regime. Bends in the flow tube have a radius of curvature greater than the flow tube radius to minimize disturbances to the flow dynamics. In all versions of the instrument, the flow tube pressure is measured with a capacitance manometer, the gas temperature with a thermocouple, and the flow velocity with a Pitot tube located downstream of the ion source and sampling orifice.

***Ion Source.*** In all of our current instrument configurations, the ion source uses a corona discharge to create the precursor ions. The corona forms between a needle held at high voltage (~2000 V) and a surrounding, grounded cup filled with a mixture of <1% CO<sub>2</sub> in O<sub>2</sub>. Free electrons from the discharge attach to oxygen to form O<sub>2</sub><sup>-</sup> ions. These react quickly with CO<sub>2</sub>, and with O<sub>3</sub> formed in the discharge, to give CO<sub>3</sub><sup>-</sup>. The source region is separated from the flow tube by a 1.2 mm diameter by 2 mm long tube to minimize transport of unwanted free radicals into the flow tube. The source gas flow of approximately 5 slm represents a minimal disturbance to the flow dynamics. Source ions are carried into the flow tube by the source gas flow and by the electric field between the needle and the source cup.

In several CIMS instruments used for air sampling from airplanes, the ion source is located upstream of the mass spectrometer sampling orifice by typically 0.5 – 1.0 m. The ions have several milliseconds to react as they flow from the ion source to the mass spectrometer. Neutral concentrations are derived from the measured ratio of reactant ion to product ion intensities, the known reaction kinetics, and the measured reaction time. We used the same configuration in our earlier SNIF-2 experiment and found that the long reaction time and the very high concentrations of exhaust species in the near-field plumes led to severe saturation problems. To reduce saturation effects, we placed the source directly opposite the mass spectrometer entrance aperture (see Fig. 1). This both reduces the reaction time and increases the total ion signal compared with an upstream ion source. The net result is no loss in sensitivity but an increased dynamic range by at least a factor of 20. We can now make accurate measurements of SO<sub>2</sub> concentrations as high as 100 ppbv. Our previous upper limit was 5 ppbv. With the present ion source placement, the reaction time is no longer well defined and cannot be used to extract neutral concentrations from the ion kinetics. Instead, we must rely on frequent in-flight calibrations in which the instrument response to a known concentration of SO<sub>2</sub> is measured. In-flight calibration reduces many uncertainties in the concentration determination, as discussed below and is now a vital part of our CIMS efforts.

***Quadrupole Mass Spectrometer.*** Once in the flow tube, the source ions react with the trace neutral species of interest. Reactant and product ions are carried across the flow tube to the sampling inlet of the mass spectrometer by the gas flow and by applied electric fields. The ions

and neutral gas enter the mass spectrometer through an orifice attached to a short sampling cone that extends several millimeters into the flow tube. The diameter of the orifice is chosen for the altitude of most interest: 50  $\mu\text{m}$  is used at ground-level atmospheric pressure, 100  $\mu\text{m}$  is routinely chosen for altitudes between 7 and 13 km, and 200  $\mu\text{m}$  has been used at altitudes around 19 km. The flow through the 100  $\mu\text{m}$  orifice at 760 torr is 4 sccm.

A supersonic expansion occurs as the gas expands through the orifice into the vacuum chamber. A commercial beam skimmer (with a 0.13 cm diameter opening located 2.5 cm behind the sampling orifice) then samples the core of the expansion. A commercial electron impact ionizer is mounted behind the skimmer, but is not used in the CIMS applications (except for diagnostic tests). The resulting beam of ions is focused into the sampling orifice of the quadrupole mass filter, mass analyzed, and detected with a pulse-counting electron multiplier. The expansion region is pumped by two 300 l s<sup>-1</sup> turbopumps, the quadrupole region is pumped by a third turbopump, and the detector region is pumped by a fourth. All four turbopumps are backed by a small, oil-free diaphragm pump. Typical pressures in the three regions are 4 x 10<sup>-3</sup> torr in the source region, 10<sup>-5</sup> torr in the quadrupole chamber, and 10<sup>-6</sup> to 10<sup>-7</sup> torr in the detector chamber.

The quadrupole mass filter is constructed in-house and consists of four 6.3 mm diameter stainless steel rods 23 cm long. The quadrupole mass spectrometer has a mass range of 10 – 135 amu and can resolve 1 amu at 135 amu. Mass analyzed ions are detected with an ETP discrete dynode electron multiplier.

All functions of the quadrupole mass spectrometer are controlled by an on-board microprocessor that is interfaced to an external laptop computer running dedicated instrument control software. Ion lens tuning, mass resolution, multiplier gain and discriminator level, the sequence of measurements, and other instrument functions can all be pre-programmed or controlled in real time through the laptop computer. The instrument cycles through the chosen measurement sequence at 96 measurements per second. For SNIF-3 and for the Lewis test chamber experiments, at least 50% of the measurement time was devoted to the SO<sub>2</sub> and HNO<sub>3</sub> species of particular interest, while the balance was dedicated to measurements of supporting peaks and occasional mass scans.

**Dryer.** When the water vapor concentration in the flow tube is high (as for airborne experiments in the troposphere or in exhaust plumes), association reactions cause the ions to be hydrated to varying degrees. In early near-field chase experiments, we observed CO<sub>3</sub><sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> ions with n as large as 6 at the upper limit of our available mass range. The shape of the distribution of hydrate ions suggested that larger clusters were also present. Product ions formed by reaction with trace neutrals can also be hydrated. Ion hydration congests the mass spectra and limits sensitivity and selectivity by spreading the ion signal to numerous masses.

To reduce the amount of hydration, we have installed a drying cell in front of the mass spectrometer sampling inlet. A heated, dry, non-reactive gas flows through the drying cell and into the flow tube. A weak electric field imposed across the cell forces the ions to move counter

to the flow and into the mass spectrometer. Collisions between the hydrated ions and the warm gas shift the hydration equilibrium so that the main ions detected are  $\text{CO}_3^-$  and  $\text{CO}_3^- (\text{H}_2\text{O})$ . Hydration of product ions is also reduced substantially and may be neglected in most cases because the hydration energies of the product ions are lower than for  $\text{CO}_3^-$ . The  $\Delta G$  of hydration for  $\text{SO}_5^-$  is 17.2 kcal/mole compared to 28 kcal/mole for  $\text{CO}_3^-$  and 18.8 for  $\text{CO}_3^- (\text{H}_2\text{O})$ .

**Real Time Calibration System.** As discussed above, neutral concentrations from CIMS measurements are often derived from measured ratios of ion intensities, the measured reaction time between the ion source and the quadrupole detector, and the known or estimated rate constants for the relevant ion-molecule reactions. Experimental uncertainties in this method include mass discrimination in the mass spectrometer, the differences between ion velocity and neutral velocity in the flow tube, and the rate constants of the ion-molecule reactions. There are at least two potential sources of error in the ion kinetics. First, the rate constants can depend on the degree of hydration of the reactant ion. In some cases, e.g. reaction (1) above for  $\text{SO}_2$ , the dependence of reaction rate on cluster size has been measured. However, for other important species, notably  $\text{HNO}_3$ , it has not. Second, the pressure dependences of the association reactions often used in CIMS detection schemes have not been measured. Other potential sources of error in the ion kinetics include the effects of secondary chemistry and the differences between kinetically-controlled and equilibrium-controlled reactions.

To circumvent these potential sources of error, we have implemented an in-situ calibration method. A calibrant gas is introduced into the flow tube through a heated inlet as close to the upstream end of the flow tube as possible. The resulting increase in the product ion signal is attributed to the calculated mixing ratio of the calibrant in the flow tube, giving the overall sensitivity of the instrument to that species. By injecting the calibration gas directly into the flow tube, we insure that the calibrant experiences exactly the same conditions of hydration, pressure, temperature, reaction rate, declustering, and wall loss as the trace gases in the atmosphere.

For the SNIF-3 and the Lewis Test Chamber experiments, we used both  $\text{SO}_2$  and  $\text{HNO}_3$  calibration gases. A mixture of 1%  $\text{SO}_2$  in helium was stored in a small gas cylinder and injected into the flow tube through a 0 – 10 sccm MKS flow controller. For the less volatile  $\text{HNO}_3$ , we used permeation tubes in a temperature controlled oven. A carrier gas flowed through the oven at all times to insure that the concentration of the nitric acid vapor did not build up. This flow was then directed either into upstream end of the flow tube during calibration periods or into the exhaust from the flow tube.

For the SNIF-3 experiments, the calibrant gases were injected directly into the flow tube at the upstream end through a heated inlet. This arrangement is shown in Fig. 1. For the Lewis test cell measurements, the calibrant gases were injected in several different locations throughout the sampling system to investigate wall losses.  $\text{SO}_2$  losses in the sampling line were negligible.  $\text{HNO}_3$  losses were only on the order of 15% and were accounted for in the data analysis.

The absolute concentration of the calibrant gas is calculated from the measured

temperature, pressure, and neutral velocity in the flow tube and from the flow of the calibrant species. A Pitot tube located on the centerline of the flow tube downstream from the quadrupole entrance aperture is used to measure the flow tube gas velocity and therefore the total gas flow. The average flow velocity is calculated from the center velocity by applying a small correction (~4%) derived from laboratory measurements of the flow profile across the flow tube. To insure complete mixing of the calibrant gas with the tube flow, a diffuser was placed across the flow tube downstream of the calibrant inlet (for the SNIF-3 experiments) or downstream of the capillary inlet carrying both the calibrant and the engine exhaust (for the test chamber experiments).

The  $\text{CO}_3^-(\text{HNO}_3)$  intensities were converted into  $\text{HNO}_3$  concentrations by injecting known flows of  $\text{HNO}_3$  mixed in  $\text{O}_2$  gas, once or twice on each altitude leg of the SONEX flights. The change in the  $\text{CO}_3^-(\text{HNO}_3)$  ion intensity during the calibration event directly gives the  $\text{HNO}_3$  sensitivity in the flow tube, assuming the temperature, pressure, and velocity of the gas in the flow tube are simultaneously measured. The calibration system consisted of a permeation tube in a 40 C temperature-controlled glass reservoir, Teflon tubing carrying  $\text{O}_2$  gas (400 std.  $\text{cm}^3 \text{ min}^{-1}$ ) through the reservoir, a three-way Teflon valve, a heated inlet into the flow tube at the point it entered the aircraft skin, and a diffuser. An  $\text{HNO}_3$  scrubbing system (a large pipe filled with nylon shavings, not shown in Fig. 1) could be placed in the flow tube through a series of valves. However, the scrubber proved not to be useful since it changed the conductance of the flow tube and hence the pressure and velocity of the air sample. In principle, compensation could be made, but the corrections were considered too large to be reliable. Thus, no background corrections were made to the data, aside from that due to imperfect mass resolution discussed above. (In the laboratory, the scrubber proved to be >80% efficient in removing  $\text{HNO}_3$  from the airstream.)

The permeation tube was made of Teflon (10-cm long, 0.3-cm OD) and filled with  $\text{HNO}_3$ . The manufacturer (Kin-Tek Laboratories, Inc., La Marque, Texas) gave the emission rate as 3992  $\text{ng min}^{-1}$  at 60 C, based on weight loss measurements over several weeks of time. During SONEX, the permeation tube was used at 40 C with often only 1/2 hr of warm-up time at the beginning of a flight. After the SONEX mission was completed, the emission rate was measured at Aerodyne Research, Inc. over two weeks time using tunable diode laser (TDL) absorption spectroscopy. The permeation tube was seen to require more than one day to reach maximum emission. The maximum emission was measured to be 5660  $\text{ng min}^{-1}$  using the TDL, at 60 C. This level of disagreement between mass-loss calibrations and actual  $\text{HNO}_3$  loss measurements has been reported previously (Huey et al., 1997). To calibrate our SONEX data, we use the TDL measurements obtained during the first 8 hr of warmup of the permeation tube, correlating the respective times between laboratory and aircraft. After 1 hr, the emission rate from the permeation tube has reached 75% of the 8-hr value. We estimate that the uncertainty associated with the  $\text{HNO}_3$  calibration is about 10%. We note that tests using deuterated nitric acid for calibration showed that the labeled acid was essentially completely converted to normal isotopic composition in the flow tube prior to detection by the CIMS, precluding its use as a calibration source.

$\text{O}_2$  gas was used as the carrier gas for the  $\text{HNO}_3$  calibrant, for convenience, being drawn from the same cylinder as was the source gas and drying gas. A Teflon 3-way valve mounted at

the  $\text{HNO}_3$  inlet to the flow tube allowed the carrier gas to flow continuously, to assure passivation of surfaces. The calibrant gas flow was diverted to the exhaust line except when the 3-way valve was activated, sending the calibrant gas onto the axis of the flow tube through a heated inlet. The heated inlet was deemed necessary because the air entering the aircraft through the sampling tube was cold (ram heated to *ca.* -10 C). The inlet was mounted just inside the skin of the aircraft so that wall losses of the calibrant  $\text{HNO}_3$  would be approximately the same as for  $\text{HNO}_3$  in the ambient air sample. The inlet was followed inside the flow tube by a diffuser made of thin stainless steel in the shape of fan blades, to mix the calibrant gas thoroughly into the air flow.

The  $\text{HNO}_3$  calibration system showed a combination of time constants. The  $\text{HNO}_3$  signal rose to 80% of its maximum within a few seconds of being valved into the flow tube and reached a steady level after 1 min. When valved back to the exhaust line, the  $\text{HNO}_3$  signal was seen initially to fall quickly, then decrease more slowly to the ambient level with a time constant of several minutes. Thus, the calibration event required at least 3 minutes at the beginning of each altitude leg.

Wall losses of  $\text{HNO}_3$  are estimated to be only 3% percent under the conditions of the SONEX flights, based on laboratory tests with a room-temperature flow tube. Laboratory tests have shown that the loss of ions to the walls of the flow tube under SONEX conditions is only 6% per meter of length, and this figure may be taken as an upper limit for  $\text{HNO}_3$  loss at the walls. In any case, the calibration procedure removes effects of wall loss from the data except for the short flow tube section extending outside the aircraft.

Our approach of deriving neutral concentrations from in-flight or in-situ calibration experiments rather than from ion ratios, reaction time, and rate constant replaces one set of experimental uncertainties with another. The uncertainties in our approach are the measurement errors in pressure, temperature, flow rates, and so on. Specific sources of uncertainty will be discussed in more detail in the results sections below. These errors are more tractable, quantifiable, and controllable than the fundamental unknowns in ion kinetics described above. As a result, the calibration approach leads to more accurate and reproducible trace gas concentration measurements.

### **Project Accomplishments:**

We have focussed our efforts in the last year on three major endeavors involving the chemical ionization mass spectrometer (CIMS) developed with this SERDP effort: data analysis of field campaigns, laboratory measurements of reaction schemes for several interesting compounds, and a thrust to reduce the sensitivity of the instrument to water.

Under the NASA part of the funding we have analyzed data from a major effort to determine the disposition of sulfur in jet aircraft fuel. Measurements taken, in-flight, 50-6000 meters behind an F16 at various engine power settings and with 8 ppm, 152 ppm and 1000 ppm fuel sulfur levels were analyzed for  $\text{SO}_2$  and nitric acid content. These data were correlated with

the data set taken using the NASA Lewis high altitude jet engine simulation chamber. A F100 engine of the same type as used in the F16 aircraft chases was powered with the same batches of fuel. Engine exhaust gas analysis were obtained at a distance of 0.3 meter from the engine exit plane. The experiments were designed to resolve the question of whether sulfur dioxide is converted to sulfuric acid within the engine or as a result of exhaust plume interactions with the atmosphere. The data give support primarily to the latter interpretation. The CIMS was the only instrument in the measurement suites with enough sensitivity to measure the sulfur dioxide produced with the low sulfur fuels. The CIMS also provided the first exhaustive measurements of nitric acid production in these engines.

We have analyzed the results from two complementary measurements of the emission index of sulfur dioxide from an advanced turbofan jet engine. In the first experiment, near field  $\text{SO}_2$  concentrations were obtained from in-flight chases. In these experiments, a NASA T-39 Sabreliner flew in close formation behind F-16 aircraft sampling their exhaust plumes at separation distances varying from 30 m to 5 km. In the second, exhaust  $\text{SO}_2$  concentrations were measured at the exit plane of the same engine in altitude test chamber at NASA's Lewis Research Center. In both sets of experiments, the fuel sulfur content, the engine power, and the altitude were systematically varied. In the flight experiments, plume age and the effect of contrail formation were also investigated. A unique aspect of these experiments was the use of the same engine type and the same fuels in the test chamber and the F-16s, allowing a direct comparison of the results.

Extractive measurements of the  $\text{SO}_2$  concentrations were made in both experiments with the Air Force Research Laboratory's chemical ionization mass spectrometer (CIMS) instrument. A significant feature of this instrument is the in-situ calibration system in which a known concentration of sulfur dioxide is injected into the instrument to determine the instrument sensitivity to that gas species. The calibrations are done under the same measurement conditions as the experiment. The calibration techniques have allowed us to obtain better than  $\pm 10\%$  precision in the measurements. This precision is reflected both in the reproducibility of  $\text{SO}_2/\text{CO}_2$  ratios in series of plume passes and also in the agreement within 9% between the EI( $\text{SO}_2$ ) results for the high sulfur fuel in both the test chamber and flight experiments. Our estimated absolute accuracy for these experiments is  $\pm 20\%$ .

In the test chamber, engine power was varied from idle to full military power, and the altitude was varied from simulated sea level to 16.7 km (55,000 ft). In the flight experiments, the range for these parameters was narrower. Engine power was varied from 80% of maximum engine rpm to full military power and altitude varied from 9.1 to 11.5 km (30,000 – 39,000 ft). The flight experiments also allowed us to investigate the effects of aircraft separation distance (plume age) and contrail formation. Within the level of precision available from the CIMS instrument, the measured  $\text{SO}_2$  emission indices did not depend on engine power, altitude, plume age, or contrail formation.

The  $\text{SO}_2$  EI depended strongly on fuel sulfur content, varying from less than 0.01 to 2.4 g  $\text{SO}_2$  /kg fuel. The fraction of fuel sulfur appearing as  $\text{SO}_2$  in the exhaust plume is a function of the measured total fuel sulfur content as well as the EI. This fraction ranged from 120 – 125 %

for the high sulfur fuels to less than 50% for the very low sulfur fuels. In the majority of cases, the 20% error bars on the absolute  $\text{SO}_2$  concentration measurements allow the measurements to be consistent with all fuel sulfur ending up as  $\text{SO}_2$ . However, there are inconsistencies between assays of fuel sulfur content between different laboratories analyzing the same fuels. These lead us to suspect that the sulfur content of the fuels may have been altered between their use in the engines and their analysis. Sources of error in the assays may have been contamination of low sulfur fuel and loss of volatile sulfur in the high sulfur cases.

Even if the fuel sulfur assays could have been performed more accurately, the 10% limits in the precision of the  $\text{SO}_2$  concentration measurements would not have allowed these experiments to measure conversion of S(IV) to S(VI) at the 10% level or lower. Because of these limitations, for SNIF-3 and the Lewis test cell measurements, the greatest utility of the CIMS  $\text{SO}_2$  measurements has been to provide an in-situ and concurrent measure of fuel sulfur content for use in modeling and aerosol analysis. For this purpose, we have provided recommended values for the fuel sulfur that are consistent with 2% conversion. The other papers in this series address whether this amount of fuel sulfur can explain the measured aerosol concentrations, volatile fractions, and size distributions. In future experiments it is clear that the S(VI) species must be measured directly in addition to  $\text{SO}_2$ , and that the assays of fuel sulfur content must be handled more carefully.

The amount of  $\text{HNO}_3$  produced is independent of the sulfur level in the fuel. The  $\text{HNO}_3$  level decreases considerably with engine temperature, presumably because  $\text{HNO}_3$  is not stable at high temperatures. Within the uncertainties in the data, there is no difference in  $\text{HNO}_3$  production for the various fuels studied. Using NASA-LeRC measurements of  $\text{EI}(\text{NO}_x)$  and  $\text{EI}(\text{NO})$ , and the AFRL measurements of  $\text{EI}(\text{HNO}_3)$ , we can calculate the  $\text{NO}_2 \rightarrow \text{HNO}_3$  conversion rate in the engine. The  $\text{NO}_2 \rightarrow \text{HNO}_3$  conversion rate is about 8% at 500 K, 6% at 600 K, 1.5% at 700 K, and drops at least a decade by 800 K. (These figures are averages over all altitudes and all fuels studied.) We attribute this decrease in the  $\text{NO}_2 \rightarrow \text{HNO}_3$  conversion rate to the thermal instability of  $\text{HNO}_3$ . There is a systematic altitude dependence in this conversion rate. A detailed examination of the data (Figs. E-3 through E-13) leads us to conclude that the altitude dependence is due either to variations in  $\text{EI}(\text{OH})$ —not measured in this test series—or due to altitude-dependent changes in combustor temperature profile and/or residence time affecting  $\text{HNO}_3$  formation from  $\text{OH}$  and  $\text{NO}_2$ .

Also, using NASA funding, we analyzed the CIMS data acquired during the NASA SONEX campaign. This campaign consisted of 15 flights in the north Atlantic flight corridor intended to measure the atmospheric effects of well aged jet exhaust plumes. These effects have been implicated in measurable changes in global cloud coverage. The CIMS instrument measured sulfur dioxide, nitric acid, and HCN during the 15 flight missions. Also onboard was the best available competing measurement technique for nitric acid, a mist chamber. The CIMS provide data comparable in quality to the mist chamber, somewhat better sensitivity, and much faster time response: 1 second vs. 10 minutes.

The various contributions to the reactive nitrogen budget in the upper troposphere were monitored during the SONEX mission by a number of instruments, one of which was the CIMS

described in this article. An overview of the observed reactive nitrogen budget has been given elsewhere (Talbot et al., 1999). Overall, during the daytime,  $\text{HNO}_3$  was found to comprise about 35% of the  $\text{NO}_y$ .  $\text{HNO}_3$  makes up a higher percentage of  $\text{NO}_y$ , when stratospheric air is mixed into tropospheric air, as seen in Figs. 5 and 6. It is worth noting that our measurements of  $\text{HNO}_3$  from a jet engine in an altitude simulation chamber (Wey et al., 1998) showed low emission indexes at cruise power: nominally 0.05 g ( $\text{NO}_2$ ) per kg of fuel, and typically 1-2% of the engine  $\text{NO}_2$  converted to  $\text{HNO}_3$  at cruise power. It is therefore not possible to measure  $\text{HNO}_3$  spikes in dilute plumes in the aircraft corridor, at least for jet engines with similar characteristics to the F-100 engine studied by Wey et al.

Our experience on the SONEX mission has taught us that a ram inlet for the CIMS system, while simple and lightweight, does not yield a steady flow in the inlet system. This results in excessive noise in the data if integration periods of less than 10 s are used. In the future, a pumped, side- or rear-facing inlet will be used, which, additionally, moots the question of aerosol evaporation during ram heating of the sampled air. Since the resulting air velocity in the inlet will be smaller than with the ram system, a heated Teflon-coated inlet is preferred. This should significantly reduce the background problem discussed above. The smaller air flow also makes a zero-air injection system reasonable, for background determinations. The CIMS instrument has undergone substantial improvement since the SONEX mission: the 6.35-mm OD quadrupole rods of the mass spectrometer have been replaced with 9.53-mm OD rods with rf focusing rods on the entrance and exit of the mass-filtering section. An rf power supply of higher frequency (2 MHz vs 1.5 MHz during SONEX) has been tested successfully. The combination of larger rods, higher frequency, and rf focusing lenses is yielding greater sensitivity and higher mass resolution than reported above.

An experiment campaign, funded by the Navy, tested the operation of the CIMS instrumentation in the highly hydrated marine boundary environment. The objective of the program is the understanding of cloud and fog formation mechanisms in the oceanic environment. This experiment also provided an opportunity to test the CIMS under simulated real-world, high moisture environments. The experiments were conducted in the Calspan Corp. atmospheric test chamber using simulated ocean environment seeded with chemical precursors and exposed to UV radiation simulating the sun. The CIMS attempted to measure sulfuric acid and methyl-sulfonic acid. The sulfuric acid proved to be less than the detection limit of the instrument, but measurements of methyl-sulfonic acid were made. CIMS is the only technique for measuring these sulfuric acid in the gas phase

In support of possible applications, water switching and back reaction rates were measured in the laboratory selected ion flow tube systems for DMS, DMSO, methanol, acetonitrile, and acetone. Proof-of-concept data was obtained on using the CIMS technique for TNT detection.

We made a substantial effort to reduce the effect of water vapor in the gas sample upon the measurement selectivity and sensitivity for typical target gases. Water vapor hydrates the target species producing a suite of mass peaks from each parent ion. Thus, the ion intensity of the parent peak is divided among the hydrated daughter masses resulting in lower net sensitivity and a more congested and complex mass spectrum. We have ameliorated the effect of the spectrum congestion by increasing the performance of the quadrupole mass spectrometer. These

hardware changes have increased the adjacent mass rejected by two to four orders of magnitude, have increased the mass resolution, enhanced the sensitivity, and increased the mass range of the instrument. These improvements are adequate for some applications, but for programs such as the marine boundary layer experiment or direct measurements of stack exhaust additional improvements are necessary.

Three separate water vapor amelioration methods were investigated: heating the sample gas, vacuum dehydration of the water, and electric field dissociation of the hydrated ion beam. The electric field dissociation method has, thus far, proved to result in degraded sensitivity of the instrument. Testing of the sample gas heating system combined with vacuum dehydration has resulted in substantial improvements in the water handling capability of the instrument. Additional improvements are expected to be forthcoming with the goal of humid, ground level air sampling probably reachable.

The Advanced Mass Spectrometry for Atmospheric Monitoring program was featured in the July 1998 SERDP newsletter. An article about the program was published in the December 1998 issue of "Environmental Science and Technology" magazine. As a result of this publicity several contacts with environmental measurement companies have been made with the goal of licensing the technology.

## **Appendix: Publications Resulting From SERDP CP-192**

### **Peer-Reviewed Journals:**

"SO<sub>x</sub> Oxidation and Volatile Aerosol in Aircraft Exhaust Plumes Depend on Fuel Sulfur Content," R. C. Miake-Lye, B. E. Anderson, W. R. Cofer, H. A. Wallio, G. D. Nowicki, J. O. Ballenthin, D. E. Hunton, W. B. Knighton, T. M. Miller, J. V. Seeley, and A. A. Viggiano, *Geophys. Res. Lett.*, **25**, 1677-1680, 1998.

"Chemical Ionization Mass Spectrometric Measurements of SO<sub>2</sub> Emissions from Jet Engines in Flight and Test Chamber Operations." D. E. Hunton, J. O. Ballenthin, J. F. Borghetti, G. S. Federico, T. M. Miller, W. F. Thorn, and A. A. Viggiano, B. E. Anderson, W. R. Cofer, III, and D. S. McDougal, C. C. Wey, *J. Geophys. Res.*, Manuscript in preparation, 1999.

"CIMS technique for the measurement of HNO<sub>3</sub> in air traffic corridors in the upper troposphere during the SONEX campaign," T. M. Miller, J. O. Ballenthin, R. F. Meads, D. E. Hunton, W. F. Thorn, A. A. Viggiano, Y. Kondo, M. Koike, and Y. Zhao, *J. Geophys. Res.*, submitted, 1999.

"Reactive Nitrogen Budget During the NASA SONEX Mission," R. W. Talbot, J. E. Dibb, E. M. Scheuer, Y. Kondo, M. Koike, H. B. Singh, L. B. Salas, A. A. Viggiano, J. O. Ballenthin, D. R. Blake, N. J. Blake, E. Atlas, F. Flocke, D. J. Jacob, and L. Jaegle, *Geophys.*

*Res. Lett.*, submitted, 1999.

"A History of Quadrupole Mass Spectrometry Research in the Earth's Atmosphere performed at the Air Force Research Laboratory," A.A. Viggiano, D. E. Hunton, and J. O. Ballenthin, *Journal of Mass Spectrometry*, in preparation, 1999.

### **Technical Reports:**

"Engine Gaseous, Aerosol Precursor and Particulate at Simulated Flight Altitude Conditions," C. C. Wey, C. Wey, D. J. Dicki, K.H. Loos, D. E. Noss, D. E. Hagen, P.D. Whitefield, M. B. Trueblood, M. E. Wilson, D. Olson, J. O Ballenthin, T. M. Miller, A. A. Viggiano, J. Wormhoudt, T. Berkoff, and R. C. Miake-Lye, NASA/TM-1998-208509. October, 1998, NASA Lewis Research Center, Cleveland, Ohio.

### **Conference Papers:**

"In-situ Mass Spectrometer Measurement of SRM Plume Composition," J. O. Ballenthin, D. E. Hunton, R. B. Gosselin, and R. Meads, AIAA-97-0527, 35th Aerospace Sciences Meeting, Reno, NV, Jan 6-10, 1997.

"Mass Spectrometric Measurements in Jet and Rocket Exhaust. (Invited)," A. A. Viggiano, J. O. Ballenthin, T. M. Miller, D.E. Hunton, W.B. Knighton, J.V. Seeley, and R.F. Meads, ACS Meeting San Francisco April 1997, Abst of Papers of the Am Chem Soc., 213: 75-ENVR, Part 1 April 13, 1997

"In-situ Measurements of Chlorine Containing Species in Solid-Fuel Rocket Motor Exhaust," R.F. Meads, J.O. Ballenthin, A. A. Viggiano, R. Gosselin, W.F. Thorn, G.R. Kirpa, D.E. Hunton, F. Federico, and J. Borghetti, AGU Fall Meeting, San Francisco Dec 1997.

"CIMS Measurements of  $\text{HNO}_3$ ,  $\text{SO}_2$  and HCN during the NASA SONEX Campaign," D. E. Hunton, J. O Ballenthin, R. F. Meads, T. M. Miller, A. A. Viggiano, J. F. Borghetti, G. S. Federico, G. R. Kirpa and W. F. Thorn, Spring AGU Meeting, May 25-29, 1998, Boston, MA.

"Measurements of Sulfur Dioxide and Nitric Acid in the Exhaust of an F-100 Jet Engine," J. O. Ballenthin, T. M. Miller, A. A. Viggiano, D. E. Hunton, J. F. Borghetti, G. S. Federico, G. R. Kirpa, and W. F. Thorn, Spring AGU Meeting, May 25-29, 1998, Boston, MA.

"CIMS Measurements of  $\text{SO}_2$  in F-16 Exhaust as a Function of Fuel Sulfur Level," J. O. Ballenthin, T. M. Miller, D. E. Hunton, R. F. Meads, J. F. Borghetti, W. F. Thorn, G. S. Federico, and A. A. Viggiano, Spring AGU Meeting, May 25-29, 1998, Boston, MA

## Published Abstracts

"Mass Spectrometric Investigations of Solid Rocket Impacts on Stratospheric Ozone," J. O. Ballenthin, A. A. Viggiano, D. E. Hunton, R. B. Gosselin, J. F. Borghetti, T. M. Miller, M. Ross, Impact of Rockets on the Stratosphere Workshop, TRW, Redondo Beach, CA, May 20, 1996.

"Mass Spectrometric Investigations of Solid Rocket Impacts on Stratospheric Ozone," J. O. Ballenthin, A. A. Viggiano, D. E. Hunton, R. B. Gosselin, J. F. Borghetti, T. M. Miller, M. Ross, Phillips Laboratory Technical Interchange Symposium, Albuquerque, NM, July, 1996.

"Rocket Impacts on Stratospheric Ozone," M. Ross and D. E. Hunton, AIAA Joint Propulsion Conference, Orlando, FL, 1-3 July, 1996.

"CIMS Measurements of  $\text{SO}_2$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  (Invited)," A. A. Viggiano, J.O. Ballenthin, W.B. Knighton, T.M. Miller, D. Hunton E. Trzcinski, J. Borghetti, W. Thorn, R. Gosselin, and F. Federico, NASA SUCCESS Science Meeting, Boulder Oct 1996.

"Advanced Mass Spectrometry for Atmospheric Monitoring," D. E. Hunton, J. O. Ballenthin, A. A. Viggiano, T. M. Miller, J. Seeley, and R. Meads, Second SERDP Symposium, Tyson's Corner, VA, Nov. 20, 1996.

"CIMS Measurements of  $\text{SO}_2$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  (Invited)," A. A. Viggiano, J.O. Ballenthin, W.B. Knighton, T.M. Miller, D. Hunton E. Trzcinski, J. Borghetti, W. Thorn, R. Gosselin, and F. Federico, NASA Test Cell Planning Meeting, Jan 1997.

"CIMS Measurements of  $\text{SO}_2$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  (invited)," A. A. Viggiano, J.O. Ballenthin, W.B. Knighton, T.M. Miller, D. Hunton E. Trzcinski, J. Borghetti, W. Thorn, R. Gosselin, and F. Federico, NASA Atmospheric Effects of Aviation Meeting, Virginia Beach Mar 1997, .

"Advanced Mass Spectrometry for Atmospheric Monitoring (invited)," D. E. Hunton, J. O. Ballenthin, A. A. Viggiano, T. M. Miller, J. Seeley, R. Meads, G. Kirpa, J. F. Borghetti, G. Federico, and W. Thorn, 3rd Annual SERDP Symposium, Washington, DC, December 3-5, 1997.

"CIMS Measurements of  $\text{HNO}_3$ ,  $\text{SO}_2$  and  $\text{HCN}$  during the NASA SONEX Campaign," D. E. Hunton, J. O Ballenthin, R. F. Meads, T. M. Miller, A. A. Viggiano, J. F. Borghetti, G. S. Federico, G. R. Kirpa and W. F. Thorn, 1998 Conference on the Atmospheric Effects of Aviation, April 27 – May 1, 1998, Virginia Beach, VA.

"Measurements of Sulfur Dioxide and Nitric Acid in the Exhaust of an F-100 Jet Engine," J. O. Ballenthin, T. M. Miller, A. A. Viggiano, D. E. Hunton, J. F. Borghetti, G. S. Federico, G. R. Kirpa, and W. F. Thorn, 1998 Conference on the Atmospheric Effects of Aviation, April 27 – May 1, 1998, Virginia Beach, VA.

“CIMS Measurements of SO<sub>2</sub> in F-16 Exhaust as a Function of Fuel Sulfur Level,” J. O. Ballenthin, T. M. Miller, D. E. Hunton, R. F. Meads, J. F. Borghetti, W. F. Thorn, G. S. Federico, and A. A. Viggiano, 1998 Conference on the Atmospheric Effects of Aviation, April 27 – May 1, 1998, Virginia Beach, VA.